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IBIS

Quarterly Report

Analysis of Cost:
Combustion Flame CVD Diamond Deposition

Contract Number: N00014-93-C2044

IBIS Associates, Inc.
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Executive Summary

IBIS Associates has developed its predictive spreadsheet model of combustion flame chemical vapor deposition (CVD) diamond film fabrication. This report explains the assumptions for combustion flame deposition theory, and shows preliminary results of the economics of this CVD diamond process.

For this report and the results contained herein, it is assumed that the transport theory model which predicts growth rates in the CVD diamond technical cost model closely predicts actual growth rates for the combustion flame technology and that the input values for variables such as the gas flow rate and substrate diameter are physically achievable.

With this assumption as the basis for cost estimation, the cost of producing 1,000 planarized polycrystalline diamond wafers at one millimeter thick is estimated in the long run to be $73 per square centimeter for the combustion flame technology.

Eighty-seven percent of the combustion flame cost is due to the deposition step, which consumes an extreme quantity of relatively expensive process gases. Overall, the material cost is 86%, the dominant factor in the total cost. Since the efficiency in capturing carbon atoms varies from about 1/10,000 to 1/100,000 for the analyses in this report, and since the cost of acetylene gas is calculated to be $1.45 per standard cubic meter, this operation has high material costs.

The combustion flame model includes kinetic theory of combustion flame deposition. According to the model based on this theory, the key factors driving the cost of thermal management diamond are the gas price, the substrate diameter, the ratio of acetylene to oxygen, and the total gas flow rate. It is shown that obtaining lower-priced acetylene has the most dramatic effect on combustion flame economics.

Alternative sources of acetylene have been analyzed. Investment into the production of lower-priced acetylene through calcium carbide hydration produces acetylene at a cost of $1.45 per standard cubic meter (SCM). Strategically locating a combustion flame CVD diamond deposition facility near an acetylene-producing plant could potentially lower the cost further, although logistic considerations minimize the likelihood of this strategy being successful. If managed, by-product acetylene would sell for about $0.92 per SCM.

To be investigated are alternative combustion flame deposition geometries. Initial expert review has revealed that the deposition geometry assumptions (i.e. nozzle:substrate diameter ratio) in the IBIS model may not be optimal for combustion flame deposition. Suggested changes in deposition geometries involve the size, shape, and distance to substrate of the combustion nozzle, as well as higher flow rates at smaller nozzle sizes.

In addition, relationships between diamond growth rate and process yield for the combustion flame technology are not incorporated into the model. It is expected that as the growth rate increases, the yield decreases; yet a specific relation between these factors is unknown. Similarly, the relationship between substrate diameter and yield requires further investigation due to the known complications with the increase of this parameter. Lastly, expert approval of the models is continually in progress.

Modeling Methods

The combustion flame CVD diamond deposition technology is characterized by a combusting oxyacetylene torch flame impinging on a cooled metal substrate in an atmospheric environment (pressure and gas composition). A complex theoretical model has been developed by Professor David Goodwin at the California Institute of Technology, and his assumptions are stated in the following paragraphs.

Model Assumptions (Goodwin memo, 1993)

The objective of this work is to develop a set of relations allowing prediction of linear growth rate, several measures of film quality, and substrate heat flux for a range of flame conditions. The geometry considered is shown in Figure 1. The following assumptions are made:

A round jet of hot combustion products exits a nozzle of inner diameter D with velocity V. The velocity profile at the nozzle exit is uniform.

The jet impinges on a substrate at normal incidence.

The pressure is at one atmosphere.

The gas consists of the combustion products of acetylene burning in oxygen. No other fuel additives, such as hydrogen, are considered.

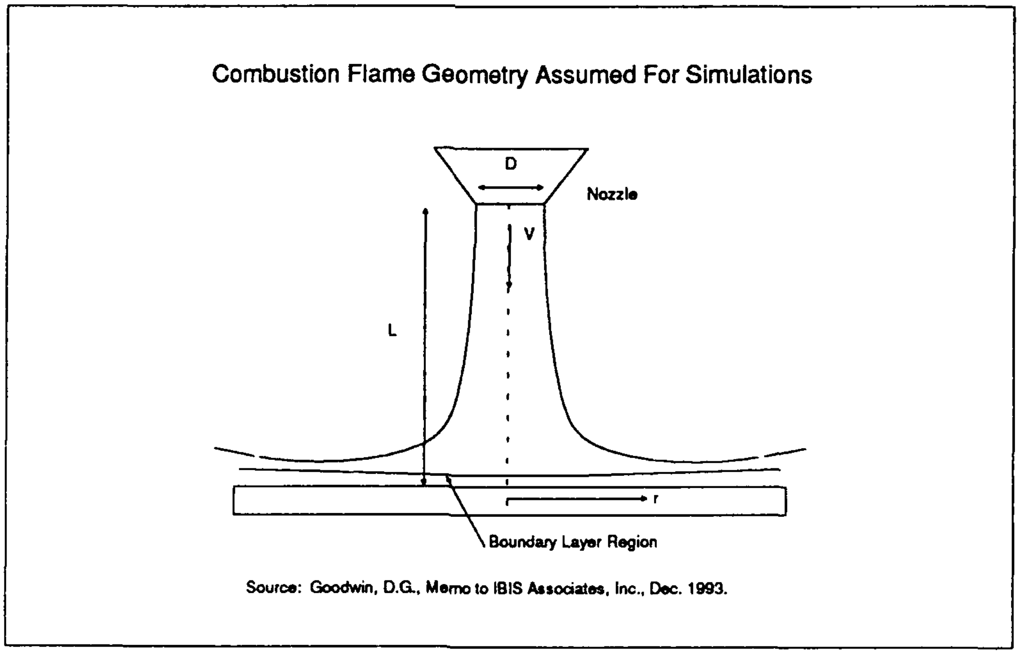

Figure 1

In the core region of the jet and outside the boundary layer, the temperature is the adiabatic flame temperature T_{ad}, and the gas composition corresponds to chemical equilibrium at this temperature.

In a flow of this type, the boundary layer thickness is nearly constant throughout the core region ($r < D/2$), and then increases at larger radii (Martin, 1977). The results presented here are strictly valid only for radii $r < D/2$. At larger r, the heat and mass transfer rates to the substrate typically decrease, although they may exhibit a second maximum for $L/D < 5$, due to the transition to turbulence (Martin, 1977). The behavior of the growth rate at radii outside the central jet is beyond the scope of the present analysis. Consequently, no attempt is made to predict the deposit diameter D_d for a given nozzle diameter D. However, a ratio $D_d/D = 1.5 - 2$ is probably reasonable for cost analysis [a diameter ratio of 1.73:1 is used in the following cost analysis].

The assumption of chemical equilibrium should be close to valid in this flow (Matsui et al, 1989; Matsui et al, 1990). Due to the high temperature, the chemical kinetics are very fast at one atmosphere. However, this assumption probably cannot be used to model substrate-stabilized flames, like those being studied at NRL and Sandia, or low-pressure flat flames, like those being studied at Caltech. These flames may require more detailed flame structure simulations. However, the qualitative trends will be very similar to those presented here.

The assumption that the gas temperature equals the adiabatic flame temperature means that heat losses are neglected. This is reasonable for a sufficiently-large jet, but may over-estimate the temperature slightly for a small jet.

Any effects oxygen may have in the surface growth mechanism are not considered. If the equilibrium assumption is valid, then these flames are highly reducing, and the oxygen concentration is negligible. Not enough research has been done to look at the effects of oxygen to meaningfully include them in a cost model at this time.

Since the gas jet is assumed to be in chemical equilibrium outside the boundary layer, the simulations may be limited to the boundary layer region. The boundary layer simulations require as input the stagnation-point strain rate parameter a, which is given by (Martin, 1977)

$$a = V/D * (1.04 - 0.034L/D). \quad (1)$$

for L/D <= 10. To a reasonable approximation,

$$a = \frac{V}{D} \, . \tag{2}$$

The characteristics of the boundary layer (including the growth rate and H concentration at the surface) depend on only two parameters: the strain rate a, and the acetylene:oxygen ratio R (assuming pressure is fixed at one atmosphere, and T = T_{ad}). The gas velocity emerging from the nozzle can be related to the standard volumetric flow rate Q by

$$V = \left(\frac{Q}{\pi D^2/4} \right) \left(\frac{T_{ad}}{273} \right) \left(\frac{\overline{M}_i}{\overline{M}_o} \right) , \tag{3}$$

where $\overline{M}_i$ is the average molecular weight of the gases before combustion, and $\overline{M}_o$ is the average molecular weight of the gases after combustion. Using this in Eq.(1) gives

$$a = \left(\frac{4\,Q}{\pi D^3} \right) \left(\frac{T_{ad}}{273} \right) \left(1.04 - 0.034 \frac{L}{D} \right) \left(\frac{\overline{M}_i}{\overline{M}_o} \right) . \tag{4}$$

Numerical Simulations

The boundary layer on the axis of symmetry was simulated numerically, using the model previously used for flame simulations (Goodwin, 1991). The velocity, temperature, and species concentration profiles are solved through the boundary layer. A total of 35 species are included in the simulation. The gas-phase chemistry consists of 161 reversible reactions, with rates taken from the literature.

The surface chemistry is a simplified form of the Harris methyl growth mechanism (Goodwin, 1993; Harris, 1990). It has been found previously that this mechanism predicts measured growth rates well (within a factor of 2) for a wide variety of different reactors, with growth rates varying over more than 2 orders of magnitude. Since this mechanism predicts trends well but may be as much as a factor of 2 off in predicting the absolute growth rate, it is recommended that the results presented here be calibrated against experimental data where possible.

Simulations have been carried out for the 5 strain rate ('a') values of 100, 400, 1600, 6400, and 25600 1/s, and for the 3 R values (where R is the ratio of acetylene:oxygen) 1.02, 1.05, and 1.1. It is believed that these values bracket those for current flame synthesis methods. For example, a flow of about 10 slm and a jet diameter of about 0.5 cm yields a strain rate of about 17,000 1/s. On the other hand, a large-area process such as that at Lockheed probably operates at significantly lower strain rate.

Results

For the present purposes, of greater interest is the growth rate, the values of [H] and [CH3] at the substrate, and the substrate heat flux. These results are provided, along with three proposed measures of quality, obtained by combining these variables. The measures of quality are:

$$Q_0 = \frac{[H]}{[CH_3]} \ . \tag{5a}$$

$$Q_1 = \frac{[H]}{G} \ . \tag{5b}$$

$$Q_2 = \frac{[H]^2}{G} \ . \tag{5c}$$

Which of these (Q_0, Q_1, or Q_2) best correlates with actual quality (e.g. thermal conductivity) is not presently known. Combustion flame industrial participants may have insights as to which is most appropriate.

Incorporation of Numerical Simulation Results

Solving for constant quality by each of the quality metrics, the data provided by Professor Goodwin allows relationships to be established between the strain rate, gas concentrations, and diamond growth rate. Cost sensitivities can be generated by varying the gas ratio or strain rate.

The data from Professor Goodwin's model provide the growth rate, atomic hydrogen concentration, and methyl concentration as a function of the strain rate and the gas ratio. However, these output parameters are not at constant quality. Assuming that the three proposed measures of quality are feasible, it is possible to specify a strain rate and gas ratio which correspond to thermal management quality diamond. An appropriate calibrating reference for this specific theory was published by Hirose et al (Hirose et al, 1990). For the gas ratio of 1.05, stagnation point strain rate of roughly 1,600 1/s, and growth rate of about 30 microns per hour mentioned in this article, the theory predicts corresponding atomic hydrogen and methyl concentrations. For the measures of quality from above, thermal management quality diamond can be recognized by a specific cutoff value. Assuming a quality mechanism with the corresponding value for thermal management diamond, either the strain rate or the gas ratio can be varied with the other being solved to maintain constant quality. Finally, the growth rate at constant quality can be determined by plugging the strain rate and gas ratio, one of which has been solved to maintain constant quality, into the growth rate relationship generated by the theory.

Sensitivity Analysis

Technical Cost Modeling permits the flexibility of performing sensitivity analyses. Using sensitivity analyses, it is possible to explore the cost implications of changing key input variables such as gas composition, production volume, material prices, product dimensions, etc. As an R&D management tool, these analyses help set development goals for cost effective manufacturing. Further, they help in long term planning, by indicating the cost savings that may be realized through scale-up. For the purpose of these sensitivity analyses it is assumed that the transport theory model which is used to predict the diamond growth rate closely predicts actual growth rates and that the input values for variables such as gas flow rate and substrate temperature are physically achievable. Presented in the following sections are the following analyses, all based on the assumption of thermal management quality diamond:

- Cost vs Acetylene:Oxygen Gas Ratio
- Cost vs Strain Rate
- Cost vs Substrate Diameter
- Cost vs Acetylene Price
- Cost and Total Gas Flow Rate vs Substrate Area
- Cost vs Substrate:Duct Area Ratio

With the exception of the last sensitivity, the ratio of substrate to duct area is held constant. This constraint is due to the geometry assumed for the combustion flame technology as modeled. The area of the gas duct is the cross-sectional area of the flame before it is affected by the flow pattern around the substrate. For a combustion flame with a corresponding duct area impinging on an infinite plane, there will be a circular region of desirable diamond and a surrounding region of unacceptable diamond. Consider the similar case of a flame impinging on a substrate of the same area. As a substrate diameter increases while the duct diameter remains constant, there is a point at which the substrate extends into this zone of unacceptable diamond. Therefore, there is a maximum substrate:duct area ratio that should not be exceeded. Experts in CVD diamond deposition suggest that this ratio is roughly 3:1 for single nozzle torches. When the substrate diameter is varied in the following analyses, the duct diameter is adjusted so that the ratio of substrate to duct area is constant at three.

Cost vs Acetylene:Oxygen Gas Ratio

As shown in Figure 2, the optimal ratio of acetylene to oxygen appears to be in the 1.04 to 1.07 range for the H^2/G and H/CH_3 measures of quality. This minimum is due to tradeoffs between the growth rate and gas flow rate: the growth rate rises faster than the gas flow rate for increasing gas ratio in the down-sloping section, causing the cost per square centimeter to decrease; at the upper end of the gas ratio range, the flow rate increases faster than the growth rate, causing the cost per square centimeter to increase. This does not appear to be true for the H/G quality measuring mechanism. For this measure of quality, the gas flow rate is always increasing faster than the growth rate, creating an increasing cost trend with gas ratio.

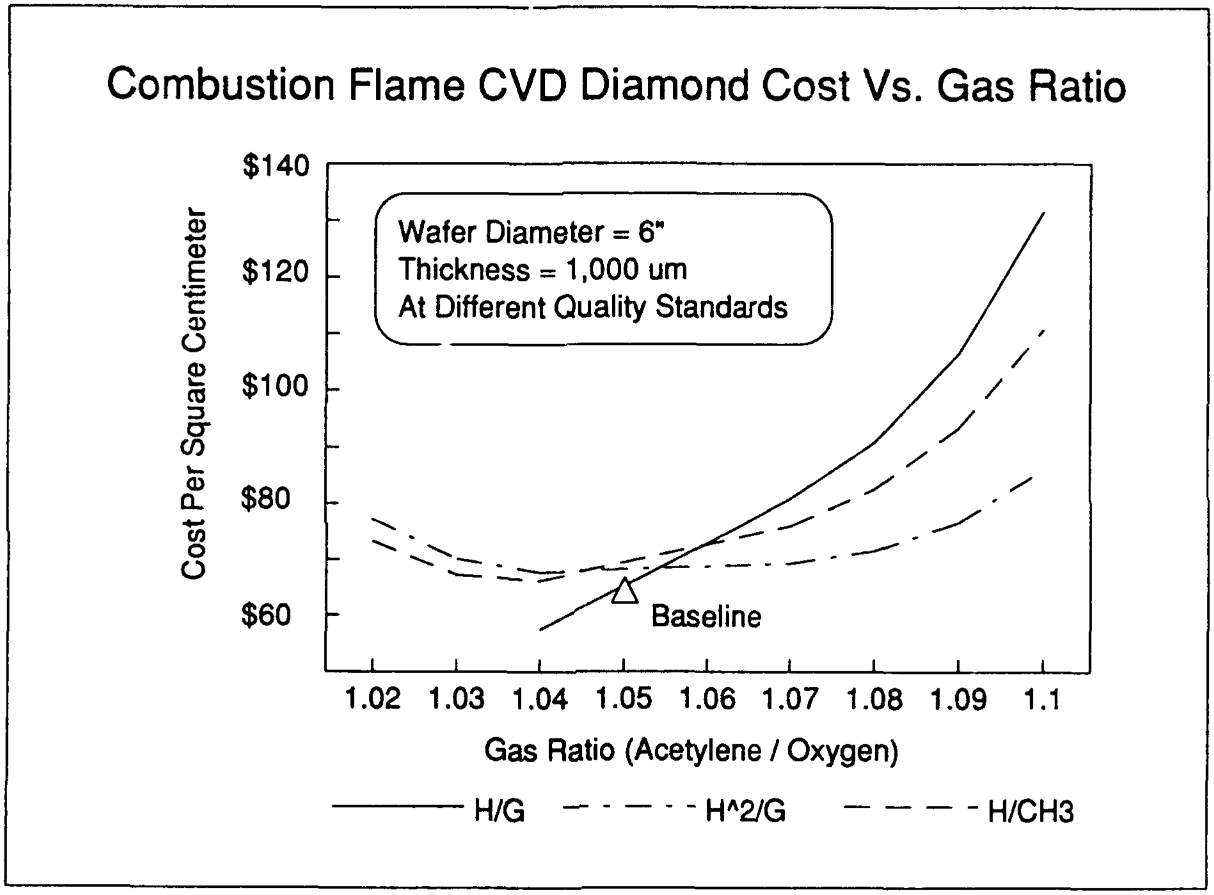

Figure 2

Cost vs Strain Rate

The trend of cost with varying strain rate, shown in Figure 3, is similar to the trend in Figure 2. Again there is an optimal range for the H^2/G and H/CH_3 measures of quality. The reason for the existence of a minimum is the same as in Figure 2. For H^2/G quality, the range of about 1,000 to 2,000 1/s produces the lowest cost diamond, while the H/CH_3 measure of quality has a cost minimum at 1,000 1/s. For the H/G quality mechanism, the flow rate is increasing faster than the growth rate with increasing strain rate, so the cost per square centimeter also rises with strain rate.

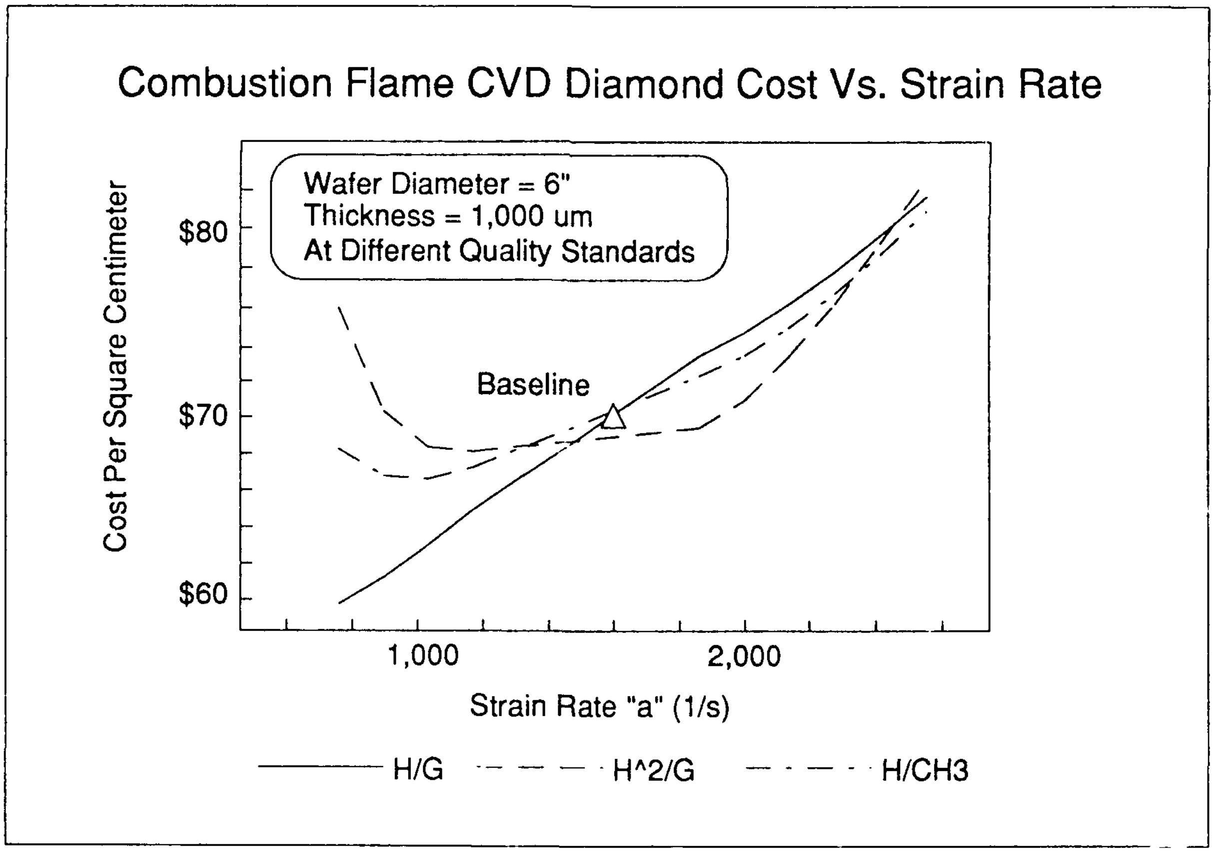

Figure 3

Cost and Total Gas Flow Rate vs Substrate Diameter

Figure 4 shows the combustion flame deposition cost per square centimeter varying with the diameter of the deposited wafer. In addition, because the duct area is changing with the substrate area to maintain a constant ratio, Figure 4 shows the total gas flow rate changing with the substrate diameter. At about seven centimeters in diameter, the cost per square centimeter of combustion flame CVD diamond reaches a minimum of roughly $46. The incorporation of the gas flow rate plot illustrates why there exists an optimum substrate diameter: as the duct area increases to maintain the substrate to duct area ratio, the volumetric gas flow rate must also increase to sustain the same strain rate parameter (same quality diamond). Therefore, the economy of scaling the substrate diameter peaks at about seven centimeters, above which the required gas flow increases the cost.

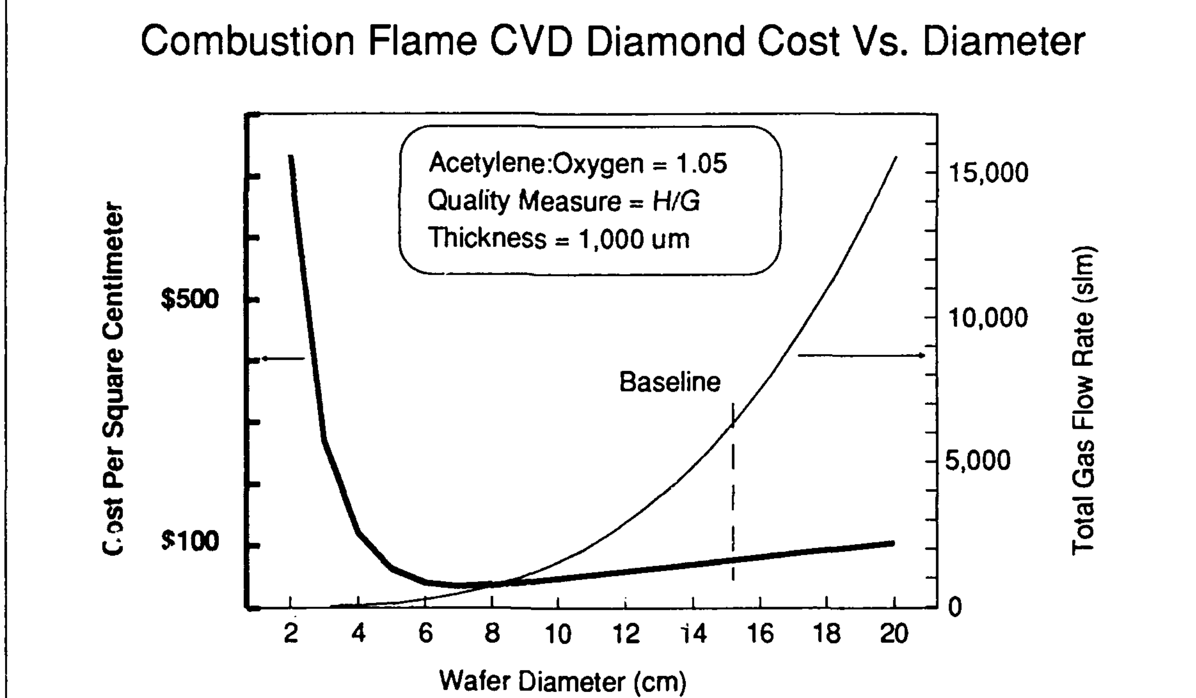

Figure 4

Cost vs Acetylene Price

For variations in acetylene price, Figure 5 depicts the opportunity for combustion flame CVD diamond cost reduction. Total diamond cost is decreased by thirty-one dollars per square centimeter for every one dollar reduction in acetylene price per standard cubic meter. At fifty cents per standard cubic meter, the total cost per square centimeter of diamond is $25. With baseline assumptions predicting a cost of $73 per square centimeter at $1.45 per standard cubic meter, it is important to decrease the price or consumption of acetylene. Subsequent sections of this report investigate alternative sources of acetylene, including in-house production using calcium carbide.

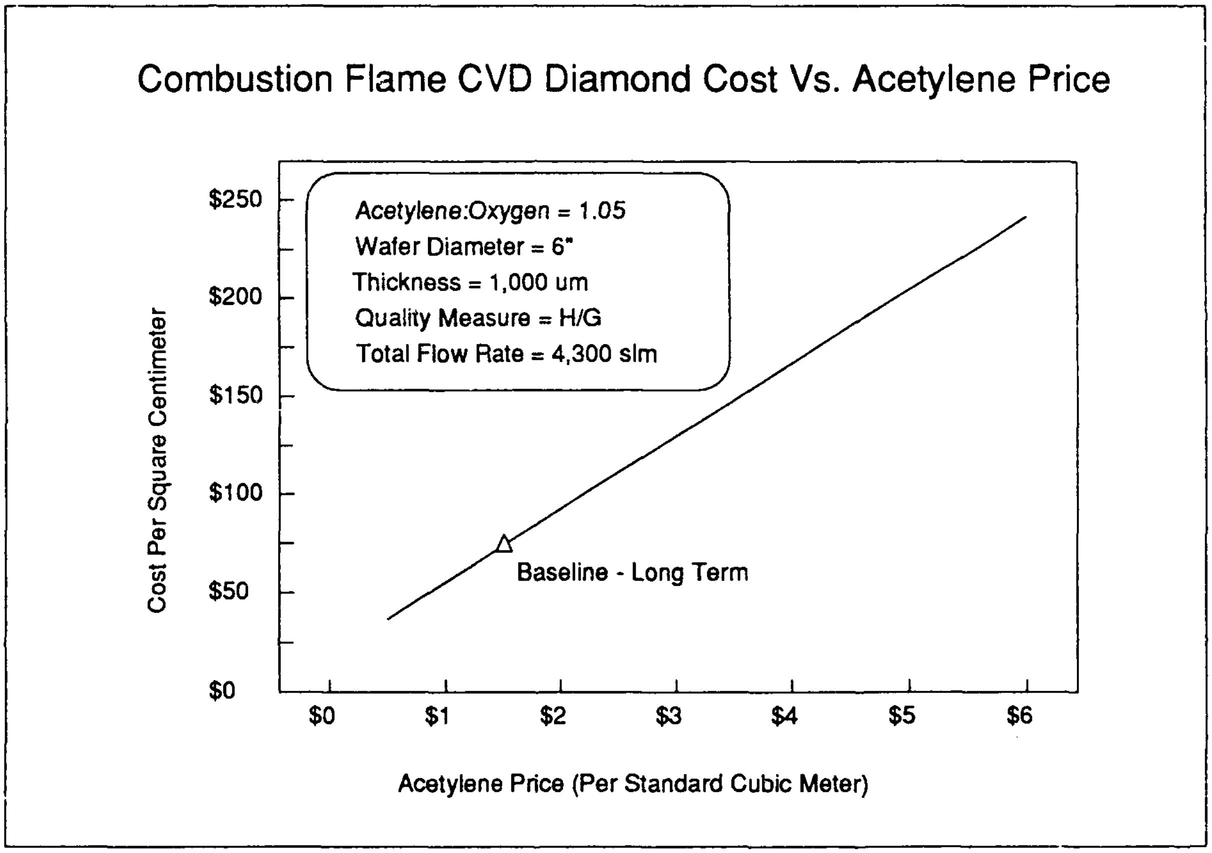

Figure 5

Cost vs Substrate:Duct Area Ratio

For the previous analyses, the substrate to duct area ratio has remained constant at three. This value has been chosen because experts in CVD diamond deposition have suggested a range of about 2.3 to 4:1 to be valid. Figure 6 shows the cost per square centimeter of diamond varying with this ratio over the range determined by deposition experts. The cost per square centimeter of combustion flame CVD diamond varies from about $109 at a ratio of 2.3:1 to $47 at a ratio of 4:1. From this data, it is evident that finding the upper limit to this ratio is critical. The mid-range baseline assumption of 3:1 forecasts a cost of $73 per square centimeter.

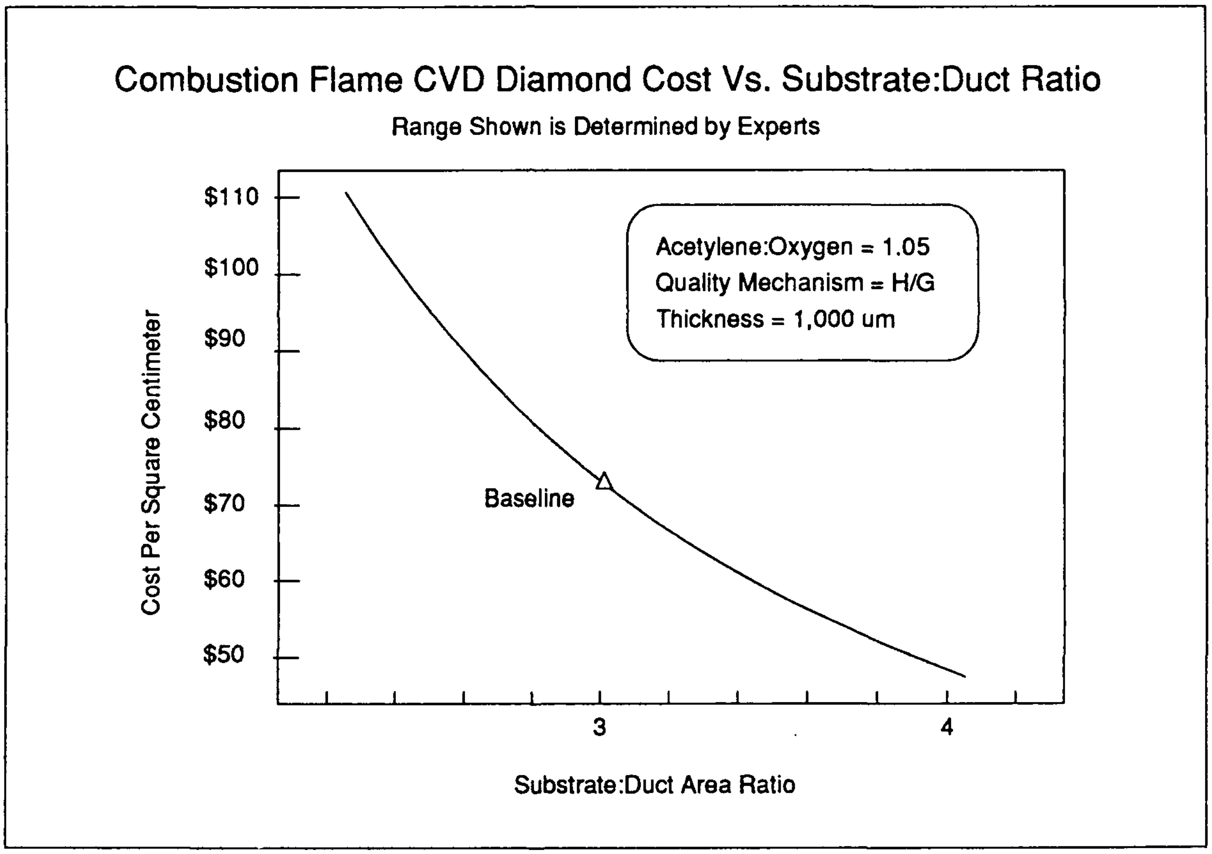

Figure 6

On-Site Acetylene Production and Acetylene Pipeline Supply

As this report points out, the driving cost factor in combustion synthesis of diamond is the high price of acetylene. Prices quoted from industrial gas suppliers for small quantities of acetylene are in the $5.30 per SCM price range. The long-term generic Combustion Flame model reports the need for 14.1 SCM per minute to produce 1000 6-inch diameter, 1mm thick diamond wafers. At $5.30 per SCM, the cost of production is $233 per square centimeter of diamond, of which the acetylene cost is 93% of the total cost. From this result it is clear that to make the Combustion Flame technology competitive with other CVD technologies on an economic basis, cheaper acetylene must be found.

A study of the possibilities for on-site acetylene production and for pipeline supplied acetylene has been undertaken. Three different acetylene production schemes and the pipeline supply scheme have been investigated and their resulting costs and caveats are reported here.

Acetylene from Calcium Carbide: Carbide to Water Method

Acetylene is produced from the reaction of calcium carbide with water. In the carbide to water method, also called wet generation, calcium carbide is dropped from a hopper into a reactor partially filled with water. The ratio of water to calcium carbide in the reactor is kept at 10:1. The acetylene and steam created from the heat of reaction rise to the top of the reactor where the acetylene is captured and purified. The reacted carbide forms calcium carbonate sludge which must be purged from the reactor. The sludge is very wet and is usually dried and then sold as lime. The reaction takes 3.1 kilograms of calcium carbide and 1.5 kilograms of water to produce 1 kilogram of acetylene and 3.6 kilograms of lime.

The cost of acetylene using this production method has been predicted to be $1.45 per SCM. 87% of this cost is due to the cost of calcium carbide.

There is only one company in the United States, RexArc, that specializes in the construction of carbide to water acetylene generators. The largest carbide to water acetylene generator that RexArc makes will produce about 3.4 SCM of acetylene per minute or 5.9 tons per day. A plant of this size will require 18 tons of calcium carbide and produce 21 tons of lime per day. In its wet form the weight of the sludge is about 3 times the weight of the lime in the sludge, that is 60 tons of sludge per day. To produce the amount of acetylene required for our baseline production assumptions would require 7 plants of this size which would require in total 126 tons of calcium carbide and would produce a total of 420 tons of sludge per day. One calcium carbide supplier, The Carbide Graphite Group, said that for such a large quantity of calcium carbide a railroad spur would need to be built to the acetylene production facility. So in addition to the cost of the production facilities it will also be necessary to account for the cost of having a railroad spur constructed.

The sludge produced in the carbide to water method presents an environmental waste problem. The sludge cannot be dumped in the form in which it comes from the reactor. Most carbide to water acetylene plants handle sludge by dumping the sludge into open tanks to evaporate the water and then recover the lime for sale, or by piping the sludge to chemical plants which can use the sludge as a neutralizing agent. Although this scheme is viable, the large amount of sludge produced by the 7 plants in our baseline model make this method impractical.

Acetylene from Calcium Carbide: Water to Carbide Method

In the water to carbide method acetylene is again produced by the reaction of calcium carbide and water. In contrast to the carbide to water method, the water to carbide method has a reactor filled with calcium carbide onto which water is allowed to drip. The proportions of reacting materials are the same as for the carbide to water method. The only important difference between these two methods is that in the water to carbide method the waste product, lime, is produced in a "dry" form rather than as a wet sludge. The dry lime can be sold more easily than the wet sludge which often must be dried before sale. The reactor, facility and railroad spur construction costs are similar to those of the carbide to water method.

The cost of acetylene using this production method has been estimated to be $1.45 per SCM. Eighty seven percent of this cost is due to the cost of the calcium carbide.

Acetylene from Carbon Gas Cracking

Another method for generating acetylene is to catalytically "crack" natural gas to form acetylene and other hydrocarbon gases. Generally, this method is used to generate high volume gases (e.g. ethylene, propylene) and the acetylene produced is only a by-product. The only companies generating acetylene by this method are petrochemical companies and they sell the acetylene for $0.95 per SCM.

Acetylene from Pipeline Supply

The high priced acetylene provided by most acetylene suppliers is delivered in cylinders. Many acetylene suppliers are willing to supply acetylene via a pipeline rather than via cylinders for much less money. The cost of the piped acetylene varies from $0.95 to $1.40 per SCM depending on the acetylene supplier, the production method used and the region of the country. The lower cost piped acetylene comes from petrochemical companies along the Gulf Coast while the higher cost acetylene comes from carbide companies in the Midwest. The lower cost acetylene is difficult to obtain. Most of the acetylene for this price is already under contract and petrochemical companies which supply it do not actively market the acetylene.

The advantages of this method are that the price of the acetylene will be the same or less than in-house production costs. Furthermore, this method does not require a large capital investment as the in-house methods do; carbide purchase and delivery is not an issue with this method; and there is no waste product to be disposed of or marketed. However, this method does have two main disadvantages. First, to receive the acetylene via pipeline the diamond production facility would need to be located within 3/4 mile of the acetylene production facility. Second, once a pipeline has been laid to an acetylene supplier, the diamond facility is tied to that one supplier; shopping around for cheaper acetylene is no longer an option.

On-Site Acetylene Production and Acetylene Pipeline Supply Summary

Three acetylene production schemes have been evaluated and costs predicted for in-house production. Also, pipeline delivered acetylene was compared with the in-house production schemes and with cylinder supplied acetylene. Of the three acetylene production schemes, only two, the carbide to water and the water to carbide methods, were possible in an in-house production setting. Of those two, the water to carbide method has a slight advantage in that the waste product can be disposed of more easily than the waste product of the carbide to water method. Both of these methods require the purchase and delivery of large amounts of raw materials and the disposal of waste products. The cost for both methods was $1.45 per SCM of which 87% of the cost was due to the cost of the calcium carbide.

The most promising acetylene acquisition scheme is the pipeline delivered acetylene. It is the lowest cost scheme evaluated; it does not require equipment investment; and it does not require raw material purchase or delivery or waste disposal. The cost for this method ranges from $0.95 to $1.40 per SCM depending on the region of the country and the acetylene supplier. The disadvantages of this method are that the diamond facility must locate within 3/4 mile of an acetylene production facility, and that the diamond facility is then tied to a single acetylene supplier. Furthermore, since acetylene generation is a by-product, rather than the focus, of the supplier's cracking operations, an uninterrupted, high quality supply stream is not necessarily guaranteed.

Summary and Conclusions

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Alternative sources of acetylene have been analyzed. Investment into the production of lower-priced acetylene through calcium carbide hydration produces acetylene at a cost of $1.45 per standard cubic meter (SCM). Strategically locating a combustion flame CVD diamond deposition facility near an acetylene-producing plant could yield still lower cost acetylene ($0.92/SCM). However, there are business reasons why this strategy may be unattractive.

To be investigated are alternative combustion flame deposition geometries. Initial expert review has revealed that the deposition geometry assumptions (i.e. nozzle:substrate diameter ratio) in the IBIS model may not be optimal for combustion flame deposition. Suggested changes in deposition geometries involve the size, shape, and distance to substrate of the combustion nozzle, as well as higher flow rates at smaller nozzle sizes.

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